

Oxidation Using Quaternary Ammonium Polyhalides. VIII.¹⁾ Oxidation of 1,4-Benzenediols with Benzyltrimethylammonium Tribromide

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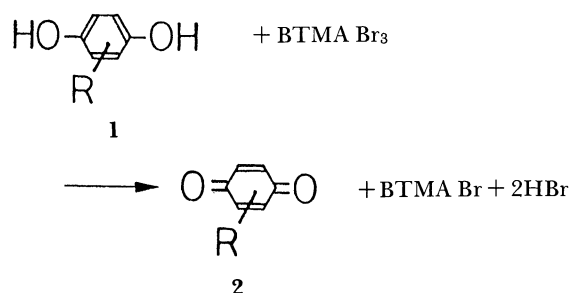
Synopsis. The reaction of 1,4-benzenediols with 1.1 equiv of benzyltrimethylammonium tribromide in dichloromethane in the presence of aqueous sodium acetate at room temperature gave 2,5-cyclohexadiene-1,4-diones in good yields. On the other hand, the reaction of 1,4-benzenediols with a large excess of the reagent in aqueous acetic acid at 40–60°C gave polybromo-substituted 2,5-cyclohexadiene-1,4-diones in good yields.

In general, 1,2- and 1,4-benzenediols are easily oxidized to 3,5-cyclohexadiene-1,2-diones (*o*-benzoquinone derivatives) and 2,5-cyclohexadiene-1,4-diones (*p*-benzoquinone derivatives), respectively. Either or both hydroxyl groups can be replaced by amino groups to give the same quinones. A number of oxidizing agents such as sodium dichromate–sulfuric acid,²⁾ manganese dioxide,³⁾ nitrous acid,⁴⁾ nitric acid,⁵⁾ iron(III) chloride,⁶⁾ lead dioxide,⁷⁾ nitrosodisulfonate,⁸⁾ (diacetoxyiodo)benzene,⁹⁾ and salcomin–oxygen¹⁰⁾ have been used. Halogens or their compounds, such as chlorine–hydrochloric acid,¹¹⁾ bromine–pyridine,¹²⁾ chlorine–sodium hypochlorite,¹³⁾ sodium hypochlorite,¹⁴⁾ sodium chlorate–vanadium oxide–sulfuric acid,¹⁵⁾ and *N*-bromosuccinimide–water,¹⁶⁾ have also been used.

In previous papers, we have reported that the reaction of 1,4-benzenediol (**1a**) with BTMA Br₃ (2 equiv) in dichloromethane–methanol gave 2,5-dibromo-1,4-benzenediol, electrophilic substitution product, in good yield.¹⁷⁾ In our further investigation regarding the synthetic utility of quaternary ammonium polyhalides, we have now found that benzyltrimethylammonium tribromide (BTMA Br₃) is a useful oxidizing agent.¹⁸⁾ In this paper we wish to report on the oxidation of 1,4-benzenediols (hydroquinone derivatives) (**1**) to 2,5-cyclohexadiene-1,4-diones (**2**) by the use of BTMA Br₃.

Results and Discussion

The reaction of **1** with 1.1 equiv of BTMA Br₃ in dichloromethane in the presence of aqueous sodium acetate at room temperature gave **2** in good yields. The results are summarized in Table (Procedure A). The reaction scheme can be represented as follows:



Scheme 1.

Generated hydrogen bromide should be removed with sodium acetate. Otherwise, disodium hydrogenphosphate (equimolar amount for BTMA Br₃) was also used instead of sodium acetate. When aqueous sodium hydroxide was used, a black oil was obtained and the desired benzoquinone derivatives could not be isolated. The end point of the reaction was detected by a decolorization of the initial orange color of the reagent.

Incidentally, when the quantity of the reagent used was less than equivalent weight for **1**, a mixture of **2** and quinhydrone derivatives, dark green needles, was obtained.

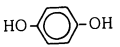
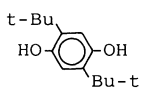
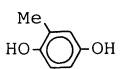
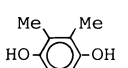
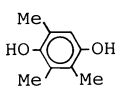
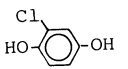
The reaction of **1** with BTMA Br₃ (1.1 equiv) in aqueous acetic acid at room temperature also gave **2** in good yields (Table: Procedure B). When the reaction of **1** was carried out with a large excess (4.0–7.5 equiv) of the reagent at 40–60°C, polybromo-substituted 2,5-cyclohexadiene-1,4-diones (**3**) were obtained in good yields (Table: Procedure B). Products **3** might be derived from **1** through the sequential reactions shown in Scheme 2.

The reaction of 2,5-di-*t*-butyl-1,4-benzenediol (**1b**) with 4–5 equiv of BTMA Br₃ gave only 2,5-di-*t*-butyl-2,5-cyclohexadiene-1,4-dione (**2b**). It can be assumed that 1,4-addition of hydrogen bromide to **2b** does not occur because of the steric hindrance of the bulky *t*-butyl group.

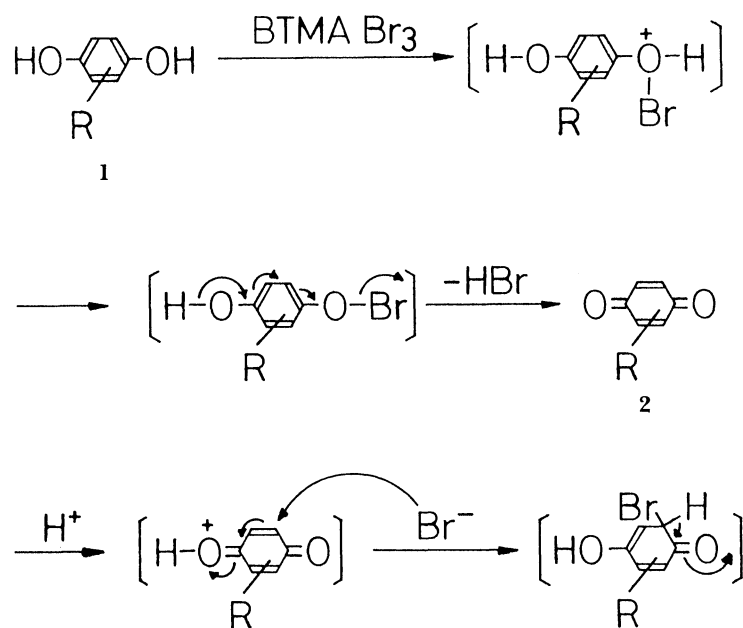
Attempts to prepare 3,5-cyclohexadiene-1,2-diones by the oxidation of 1,2-benzenediols (catechol derivatives) with BTMA Br₃ failed.

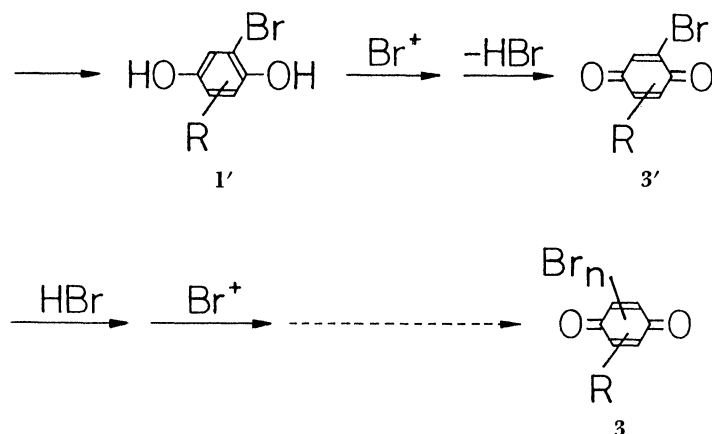
We believe that, although many other procedures for the oxidation of **1** to **2** or **3** have been reported, our methods using BTMA Br₃ are characterized by simple operation, mild conditions, and good product yields.

Table 1. Oxidation of 1,4-Benzenediols with BTMA Br₃

Substrate 1	Procedure A ^{a)} or B ^{b)}	Molar ratio BTMA Br ₃ /1	Reaction conditions		Product ^{c)} 2 or 3	Yield ^{d)} %
			Temp/°C	Time		
 (1a)	{ A B	1.1	R.t.	2 h	2a	Quant.
		1.1	R.t.	5 min	2a	Quant.
		7.5	60	5 h	3a	88
 (1b)	{ A B	1.1	R.t.	5 h	2b	Quant.
		1.1	R.t.	10 min	2b	Quant.
		4.5	60	24 h	2b	94
 (1c)	{ A B	1.1	R.t.	2 h	2c	Quant.
		1.1	R.t.	10 min	2c	96
		6.0	60	5 h	3c	94
 (1d)	{ A B	1.1	R.t.	2 h	2d	Quant.
		1.1	R.t.	10 min	2d	Quant.
		4.5	60	5 h	3d	Quant.
 (1e)	{ A B	1.1	R.t.	2 h	2e	Quant.
		1.1	R.t.	10 min	2e	93
		4.0	40	5 h	3e	Quant.
 (1f)	A	1.1	R.t.	10 h	2f	90

a) **A**: Oxidation was carried out in CH₃COONa aq/CH₂Cl₂. b) **B**: Oxidation was carried out in CH₃COOH aq.
 c) Products were characterized by comparing ¹H NMR spectra and mp with those of authentic samples or reported data.
 d) Yield of isolated product.





Scheme 2.

Experimental

Oxidation of 1,4-Benzenediol (1a) with BTMA Br₃-CH₃COONa aq. Representative procedures are as follows. To a solution of sodium acetate hydrate (CH₃COONa·3H₂O) (0.82 g, 6 mmol) in water (20 ml) was added 1a (0.22 g, 2 mmol) and a solution of BTMA Br₃ (0.86 g, 2.2 mmol) in dichloromethane (10 ml). The mixture was stirred at room temperature for only 2 min until the initial orange color faded. Then, the water layer was filtered through wet filter paper. The separated organic layer was washed with water and dried over MgSO₄, filtered, and evaporated in vacuo give 2,5-cyclohexadiene-1,4-dione (*p*-benzoquinone) (2a) as a yellow needles; yield 0.22 g (quant.); mp 113–115°C (lit.¹⁹ mp 114.6–115.6°).

Oxidation of 2,5-Di-*t*-butyl-1,4-benzenediol (1b) with BTMA Br₃-AcOH aq. BTMA Br₃ (0.86 g, 2.2 mmol) was added into a solution of 1b (0.44 g, 2 mmol) in acetic acid (5 ml)–water (10 ml). The mixture was stirred at room temperature for 10 min until the initial orange red color faded. The reaction mixture was extracted with dichloromethane (10 ml×3) and the organic layer was washed with water and dried over MgSO₄, filtered, and evaporated in vacuo to give 2,5-di-*t*-butyl-2,5-cyclohexadiene-1,4-dione (2b) as yellow needles; yield 0.44 g (quant.) mp 153–154°C (lit.²⁰ mp 153°C).

Preparation of 3,5,6-Tribromo-2-methyl-2,5-cyclohexadiene-1,4-dione (3c). BTMA Br₃ (4.68 g, 12 mmol) was added into a solution of 2-methyl-1,4-benzenediol (1c) (0.25 g, 2 mmol) in acetic acid (5 ml)–water (10 ml). The mixture was stirred at 60°C for 5 h, and then allowed to stand at room temperature. Water (100 ml) was added into the reaction mixture and the mixture was cooled in an ice bath. Deposited yellow solids were filtered and washed with water. The filtrate and washings were combined and extracted with ether (20 ml). The ether solution was evaporated in vacuo to give 3c as yellow plates; yield 0.68 g (94%); mp 243–245°C (lit.²⁰ mp 233°C).

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